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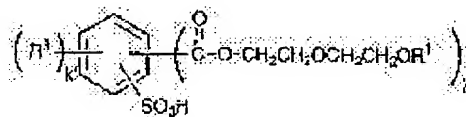
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(54) AQUEOUS POLYANILINE COMPOSITION AND PRODUCTION THEREOF

(57)Abstract:

PURPOSE: To provide an aqueous polyaniline composition which contains a polyaniline or its derivative, a protonic acid dopant, a copolymerized polyester and water and is suitable for forming an electrically conductive coating film layer because it can be dissolved or dispersed in an aqueous solvent in a dope form.

CONSTITUTION: This composition comprises (A) a polyaniline and/or its derivative, (B) a protonic acid dopant (preferably a compound of the formula (R1 is H, a 2-12C alkyl; R1' is H, an aryl; K is 1-5; K' is 0-4; where K+K'=5), (C) a copolymerized polyester and (D) water. This composition is obtained by dissolving or dispersing components A and B in water and/or a solvent soluble in water, and dissolving or dispersing component C in water and/or a solvent soluble in water, then mixing these solutions or dispersion. The component C is preferably obtained from the polycarboxylic acid component containing 2-35 mole % of a metal sulfonate group-containing aromatic dicarboxylic acid and 65-98 mole % of no metal sulfonate group-containing polycarboxylic acid and the glycol component.



LEGAL STATUS

<http://www19.ipdl.jpo.go.jp/PA1/result/detail/main/wAAQBaGGpDA408120167P1.htm>

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CLAIMS

[Claim(s)]

[Claim 1] The drainage system poly aniline constituent which comes to contain the poly aniline and/or its derivative (A), a proton acid dopant (B), copolymerized polyester (C), and water (D).

[Claim 2] The drainage system poly aniline constituent according to claim 1 which is copolymerized polyester (C) which the polycarboxylic acid component of copolymerized polyester (C) becomes from dicarboxylic acid 65 - 98-mol % and sulfonic-acid metal salt content aromatic series dicarboxylic acid 2 - 35-mol % which does not contain a sulfonic-acid metal salt, and a polyol component becomes from a glycol.

[Claim 3] The drainage system poly aniline constituent which comes to contain a water-soluble organic solvent (E) and/or a surfactant (F) further in a drainage system poly aniline constituent according to claim 1 or 2.

[Claim 4] The drainage system poly aniline constituent according to claim 1 to 3 which the poly aniline and/or its derivative (A), a proton acid dopant (B), copolymerized polyester (C), water (D), the water-soluble organic solvent (E), and the surfactant (F) contain at a following rate.

(A)/(B)/(C)/(D)/(E)/(F)

= 0.01-60/(0.01-60)/(0.01-60)/(5-99.97)/(0-90)/(0-5) (weight ratio)

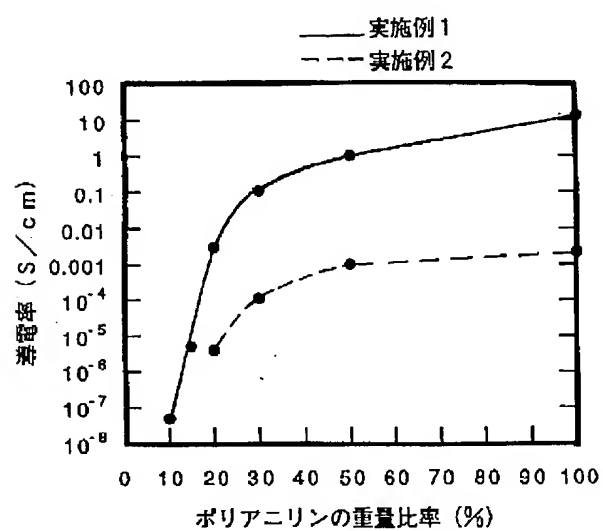
[Claim 5] The manufacture approach of the drainage system poly aniline constituent according to claim 1 to 4 characterized by including the following process.

(1) The process which makes water and/or a water-soluble solvent dissolve or distribute the poly aniline and/or its derivative (A), and a proton acid dopant (B).

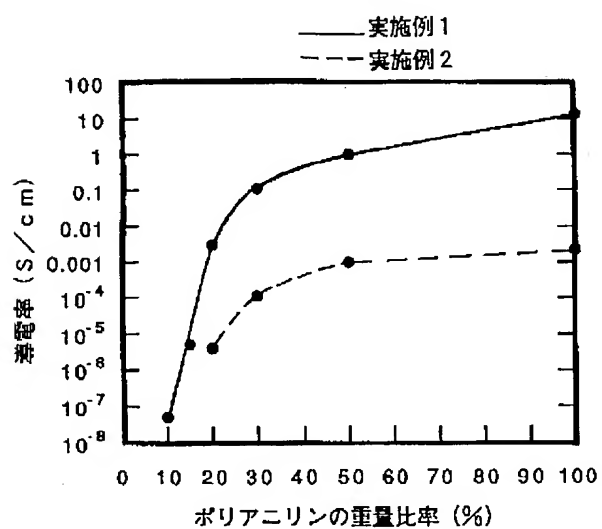
(2) The process which makes water and/or a water-soluble solvent dissolve or distribute copolymerized polyester (C).

(3) The process which mixes the solution or dispersion liquid prepared by the above (1) and (2).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the drainage system poly aniline constituent which comes to contain the poly aniline dissolved or distributed to the partially aromatic solvent of water or a water-soluble solvent in the state of a dope (condition that a dopant lives together), or its derivative and copolymerized polyester, and this constituent. Since the constituent containing the poly aniline and copolymerized polyester of this invention dissolves or distributes to a drainage system solvent in the state of a dope, the drainage system solution or dispersion liquid of this constituent is applied to a base material, it can fabricate by the simple method of drying on a film, a sheet, a coat, etc., and these have high conductivity, the outstanding antistatic nature and transparency, stability, reinforcement, and solvent resistance.

[0002] The constituent of this invention is effective as antistatic agents, such as a resin fabrication article, plastic film, a synthetic paper, and fiber. Although a resin fabrication article is a fabrication article obtained by carrying out size enlargement using heat and/or a solvent using thermoplasticity and/or thermosetting resin and a film, a synthetic paper, and fiber are also contained in a wide sense, the thing of configurations other than these is contained in this invention. Moreover, what processes it further and is obtained is contained, using a primary fabrication article as a material.

[0003] Although plastic film is usually processed further and it is used for a ceramic mold releasing film, a chip carrier film, a sensible-heat type and the film for electrostatic transparence record, the film for magnetic-recording ingredients, a photographic film, the dry film for ** material, a conductive package film, a tracing film, the film for sensitive material, etc., the poly aniline and the copolymerized polyester content constituent of this invention are effective also as these antistatic agents.

[0004] Moreover, the constituent of this invention is used for the antistatic agent of the synthetic paper of polyester and a polypropylene system. As fiber, there are a natural fiber, a chemical fiber, a synthetic fiber, an inorganic fiber, etc., there are specifically inorganic fibers, such as synthetic fibers, such as chemical fibers, such as natural fibers, such as cotton, hemp, wool, and silk, and rayon, and polyester polyamide acrylic polyethylene polypropylene polyurethane, and a glass fiber, a carbon fiber, etc., and the constituent of this invention is effective also as these antistatic agents. It is effective for electrification prevention of the material especially used for the product for clean rooms, for example, a fatigue dress, shoes, a carpet, a chair, a desk, etc.

[0005] Since the outstanding corrosion prevention effectiveness is shown when the constituent of this invention is furthermore covered with the same approach on a surface of metal, it is used also as an anticorrosive paint.

[0006]

[Description of the Prior Art] The conductive organic polymer which contains electrolyte ion as a dopant is obtained by carrying out the chemistry oxidation polymerization of the aromatic compounds, such as an aniline, a pyrrole, and a thiophene, using a chemistry oxidizer. However, generally, non-** and since it was insoluble, the conductive organic polymer was difficult fabrication, and it had become a practically serious failure.

[0007] About the poly aniline, the approach (JP,3-28229,A) a dedope poly aniline (poly aniline with which a dopant does not coexist) processes a moldings into a polar organic solvent of a certain kind using a meltable thing is proposed. However, according to this approach, two processes of the process which dopes proton acid were required for the process which acquires a Plastic solid from a dedope poly aniline, and the acquired Plastic solid, and it was complicated.

[0008] The approach (WO No. 22911 [92 to] official report) of solubilizing a dope poly aniline (poly aniline

with which a dopant coexists) is proposed. However, this approach was harmful and had problems, such as using a strong corrosive solvent and using superfluous corrosive proton acid as a dopant.

[0009] Moreover, the method (JP,3-285983,A) of dissolving a dope poly aniline in the polar organic solvent which added ammonia or an volatile amine is also proposed. However, this approach also had the trouble that sometimes harmful ammonia or amine gas occurred. [removal / after shaping / solvent]

[0010] The water-soluble poly aniline (JP,5-178989,A) of the self-doping mold which carried out direct coupling of the sulfonic-acid residue which furthermore serves as a dopant to the polymer frame is also proposed. However, this poly aniline had the complicated production process, and the problem was in the cost side.

[0011] On the other hand, the approach (JP,2-69525,A) of carrying out the chemistry oxidation polymerization of an aniline or its derivative under existence of a base material is proposed as an approach of making the thin film of the poly aniline forming. However, this approach was unsuitable to industrial large scale production. Thus, there were many troubles in-using the poly aniline industrially.

[0012]

[Problem(s) to be Solved by the Invention] The result studied wholeheartedly that this invention persons should develop the drainage system poly aniline constituent suitable for dissolving or distributing, applying to a drainage system solvent, and forming a conductive film in the state of a dope, making a dope condition poly aniline live together in copolymerized polyester, especially sulfonic-acid metal salt content aromatic series dicarboxylic acid -- 2-35-mol % -- by making a dope condition poly aniline live together in the included copolymerized polyester It came to complete a header and this invention for all the conventional troubles being solvable.

[0013]

[Means for Solving the Problem] That is, this invention is a drainage system poly aniline constituent which comes to contain the poly aniline and/or its derivative (A), a proton acid dopant (B), copolymerized polyester (C), and water (D). Moreover, it is the drainage system poly aniline constituent which is a drainage system poly aniline constituent with which the polycarboxylic acid component of this copolymerized polyester (C) consists of dicarboxylic acid 65 - 98-mol % and sulfonic-acid metal salt content aromatic series dicarboxylic acid 2 - 35-mol % which does not contain a sulfonic-acid metal salt as the desirable mode, and a polyol component consists of a glycol, and which is copolymerized polyester (C), and comes to contain a water-soluble organic solvent (E) and/or a surfactant (F) further in this drainage system poly aniline constituent. And the poly aniline and/or its derivative (A), a proton acid dopant (B), copolymerized polyester (C), water (D), a water-soluble organic solvent (E), and a surfactant (F) are related with the drainage system poly aniline constituent contained at a following rate as a desirable mode of the configuration of this drainage system poly aniline constituent.

(A)/(B)/(C)/(D)/(E)/(F)

= 0.01-60/(0.01-60)/(0.01-60)/(5-99.97)/(0-90)/(0-5) (weight ratio)

[0014] Furthermore, this invention relates to the manufacture approach of the drainage system poly aniline constituent characterized by including the following process about this drainage system poly aniline constituent again.

(1) The process which makes water and/or a water-soluble solvent dissolve or distribute the poly aniline and/or its derivative (A), and a proton acid dopant (B).

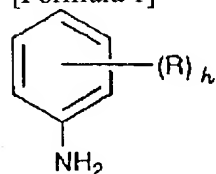
(2) The process which makes water and/or a water-soluble solvent dissolve or distribute copolymerized polyester (C).

(3) The process which mixes the solution or dispersion liquid prepared by the above (1) and (2).

[0015] The poly aniline which is one component of the poly aniline constituent of this invention, and/or its derivative (A) carry out the oxidation polymerization of the aniline shown by the following formula (1), or its derivative, and are obtained.

[0016]

[Formula 1]



式 (1)

even when the inside of a formula and R are the same -- differing -- **** -- respectively -- hydrogen and an alkyl group -- An alkenyl radical, an alkoxy group, an alkanoyl radical, an alkylthio group, an aryloxy group, An alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, An alkyl sulfinyl group, an alkoxyalkyl group, an alkyl sulfonyl group, An alkoxy carbonyl group, the amino group, an alkylamino radical, a dialkylamino radical, an aryl thio radical, an aryl sulfinyl group, an aryl sulfonyl group, a carboxyl group, a halogen, a cyano group, a halo alkyl group, a nitro alkyl group or a cyano alkyl group, and h show the integers from 0 to 5.

[0017] As desirable R, the alkyl group, the hydrogen, an alkoxy group, an aryl group, a cyano group, a halogen, an aryloxy group, etc. of carbon numbers 1-5 are mentioned.

[0018] As the example, an aniline, ortho toluidine, meta toluidine, o-ethylaniline, m-ethylaniline, an o-ethoxy aniline, m-butyl aniline, m-hexyl aniline, m-octyl aniline, 2, 3-dimethylaniline, 2, 5-dimethylaniline, 2, 5-dimethoxy aniline, o-cyano aniline, 2, 5-dichloro aniline, 2-BUROMO aniline, 5-chloro-2-methoxyaniline, 3-phenoxy aniline, etc. are mentioned.

[0019] As an oxidizer used in case the oxidation polymerization of the above-mentioned poly aniline or the above-mentioned aniline derivative is carried out, although a ammonium peroxydisulfate, a hydrogen peroxide, secondary salt-ized iron, etc. are mentioned, for example, it is not limited to these. A ammonium peroxydisulfate is mentioned as what is used preferably.

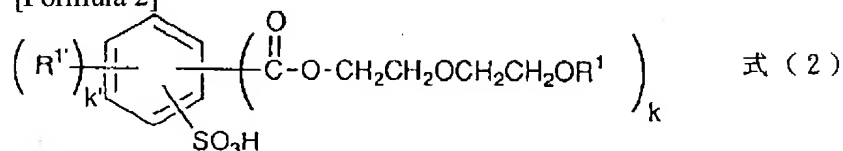
[0020] In this invention, the poly aniline and/or the desirable operating rate of the derivative (A) are 0.04 - 20 % of the weight more preferably 0.01 to 60% of the weight to the whole drainage system poly aniline constituent of this invention. If conductivity falls at less than 0.01 % of the weight, and the operating rate is lacking in practicality and exceeds 60 % of the weight, the reinforcement when considering as a thin film and flexibility will fully be hard to be acquired.

[0021] In the proton acid dopant (B) used for this invention, 4.0 or less proton acid of a dopant is [an acid dissociation constant electric dissociation exponent value] desirable. As such a dopant, although polymer acids, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, a nitric acid, and perchloric acid, benzenesulfonic acid, p-toluenesulfonic acid, m-nitro benzoic acid, a trichloroacetic acid and an organic acid as further shown in the following formulas, polystyrene sulfonate, a polyvinyl sulfonic acid, and a polyvinyl sulphate, can be mentioned, it is not limited to these.

[0022] As a desirable dopant, it is shown in the following formulas, and since it dissolves or is easy to distribute water and an organic solvent, the poly aniline doped by these dopants is suitable for mixing with copolymerized polyester (C) in liquid.

[0023]

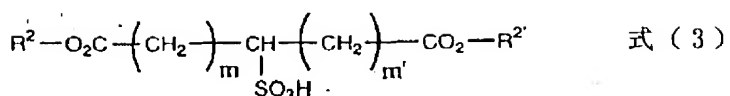
[Formula 2]



among the formula, 1 to 15, when the alkyl group of 2 to 12, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group are shown preferably and more than one exist, even if R1 has hydrogen or a the same carbon number, it may differ. R1' shows hydrogen, an alkyl group, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, an alkylthio alkyl group, an alkoxy group, an alkylthio group, an alkyl sulfinyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen, and when more than one exist, even if the same, they may differ. As desirable R1', it is hydrogen, an alkyl group, an aryl group, an alkoxyalkyl group, an alkylthio alkyl group, an alkoxy group, an alkylthio group, an alkyl sulfinyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, and a hydroxy group, and they are hydrogen, an alkyl group, an aryl group, an alkoxyalkyl group, an alkylthio alkyl group, an alkoxy group, an alkylthio group, an alkyl sulfinyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, and a hydroxy group still more preferably. k -- 1 to 5 -- desirable -- the integer of 2 to 4 -- being shown -- the integer of k'0 to 4 -- being shown -- k+k'=5.

[0024]

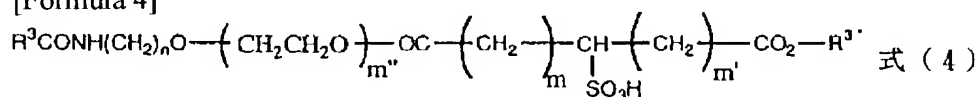
[Formula 3]



the inside of a formula, R2, and R2' are the same -- or you may differ and hydrogen or a carbon number shows the alkyl group of 5 to 15, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group. As for desirable R2 and R2', a carbon number shows the alkyl group of 5 to 15, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group. m and m' shows the integer of 0 to 5. Preferably, m+m' is 1 to 8.

[0025]

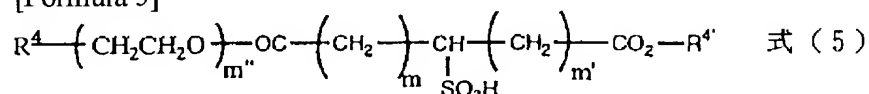
[Formula 4]



the inside of a formula, R3, and R3' are the same -- or you may differ and hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group. As for desirable R3 and R3', a carbon number shows the alkyl group of 7 to 20, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group. m, m', and m'' show the integer of 0 to 5. Desirable m+m' is 1 to 8 and desirable m'' is 2 to 5. n shows the integer of 1 to 5.

[0026]

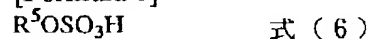
[Formula 5]



(As for R4, hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, an alkylthio alkyl group, and an alkoxy group among a formula.) Desirable R4 The alkyl group of carbon numbers 7-20, an alkoxyalkyl group, an aryloxy alkyl group, an alkylthio alkyl group, and an alkoxy group are shown. As for R4', hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group, and desirable R4' shows the alkyl group of carbon numbers 7-20, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group. m, m', and m'' show the integer of 0 to 5. Desirable m+m' is 1 to 8 and desirable m'' is 2 to 5.

[0027]

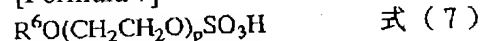
[Formula 6]



(As for R5, a carbon number shows the alkyl group of 20 to 40, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group among a formula.) Desirable R5 An alkyl group, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group are shown.

[0028]

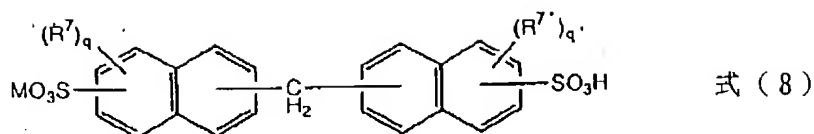
[Formula 7]



(As for R6, a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group among a formula.) Desirable R6 A carbon number shows the alkyl group of 7 to 20, an alkoxyalkyl group, an aryloxy alkyl group, and an alkylthio alkyl group. p -- 1 to 5 -- the integer of 2 to 5 is shown preferably.

[0029]

[Formula 8]



(M shows the cation (except for a proton) of monovalence, such as sodium ion, potassium ion, and ammonium ion, among a formula.) R7 and R7' show hydrogen, an alkyl group, an alkenyl radical, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, an aryloxy alkyl group, an alkylthio alkyl group, an alkoxy group, an alkylthio group, an alkyl sulfinyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen, and when more than one exist, even if the same, they may differ. Desirable R7 and R7' show hydrogen, an alkyl group, an alkoxyalkyl group, an aryloxy alkyl group, an alkylthio alkyl group, an alkoxy group, an alkylthio group, an alkyl sulfinyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen. q and q' shows the integer of 1 to 6.

[0030] Although it does not interfere even if the equivalent is sufficient as the amount of the proton acid radical of a dopant and it applies it superfluously to the poly aniline (A), it is 1-3Eq preferably.

[0031] The method of performing addition and a polymerization reaction is mentioned in the solution containing the solution which especially limitation does not have as an approach of obtaining the poly aniline constituent of this invention, for example, contains an oxidizer and proton acid in the mixture of the solution of an aniline and/or its derivative, and proton acid, or suspension, or an oxidizer. A proton acid dopant (B) may be added and doped at the time of the oxidation polymerization of an aniline and/or its derivative. Moreover, by processing the dope poly aniline obtained by the above-mentioned approach by bases, such as aqueous ammonia, it dedopes, it processes with desired proton acid again to this dedope poly aniline, and is good also as a dope poly aniline. The polymerization of an aniline and/or its derivative is carried out on the polymerization conditions usually performed. For example, within the limits of 48 hours, under ordinary pressure, reaction temperature makes a reaction mixture agitate and performs reaction time from 30 minutes between -10 degrees C and 40 degrees C.

[0032] The desirable operating rate of the proton acid dopant (B) used for this invention is 0.04 - 20 % of the weight more preferably 0.01 to 60% of the weight to the whole drainage system poly aniline constituent of this invention. If conductivity falls at less than 0.01 % of the weight, and the operating rate is lacking in practicality and exceeds 60 % of the weight, the reinforcement when considering as a thin film and flexibility will fully be hard to be acquired.

[0033] In order to make stability dissolve or distribute the poly aniline used for this invention and/or its derivative (A), and a proton acid dopant (B) to a drainage system solvent, it is required to make copolymerized polyester (C) live together. A drainage system solvent means a mixed solvent with a water independent or a water-soluble organic solvent here. The polycarboxylic acid component in copolymerized polyester has desirable 2-35 mol thing which it is % and a polyol component becomes from a glycol of 65-98 mol % and sulfonic-acid metal salt content aromatic series dicarboxylic acid of dicarboxylic acid which does not contain a sulfonic-acid metal salt. making the rate of sulfonic-acid metal salt content aromatic series dicarboxylic acid into 2-35-mol % in this polycarboxylic acid component -- desirable -- more -- desirable -- 5-35-mol % -- further -- desirable -- 7-35-mol % -- it is 10-35-mol % most preferably.

[0034] As for the dicarboxylic acid component which does not contain the sulfonic-acid metal salt used for copolymerized polyester (C), carbon numbers, such as aromatic series dicarboxylic acid, such as a terephthalic acid and isophthalic acid, an adipic acid, and an azelaic acid, can use the aliphatic series of 2 to 40 or/, and alicycle group dicarboxylic acid. As a glycol component, carbon numbers, such as ethylene glycol, a diethylene glycol, a polyethylene glycol, neopentyl glycol, a cyclohexane -1, and 4-dimethanol, can use the glycol of 2 to 40.

[0035] Furthermore, the polycarboxylic acid of three or more functional groups and polyol can be used as a copolymerization component in the range to which the solubility of copolymerized polyester (C) does not fall. For example, polyols, such as polycarboxylic acid, such as trimellitic acid and pyromellitic acid, a glycerol, and pentaerythritol, are mentioned. The polymerization method for compounding the copolymerized polyester (C) of this invention should just apply to the polymerization method of usual copolymerized polyester correspondingly.

[0036] Although the conductivity of a constituent becomes high so that there are generally many poly anilines

in a constituent and/or rates of the derivative (A), the reinforcement when considering as a thin film, flexibility, transparency, etc. tend to fall. The copolymerized polyester (C) used for this invention mainly improves such a fault, and mainly gives many properties, such as reinforcement, flexibility, and adhesion, to the thin film and coat which are obtained from the drainage system poly aniline constituent of this invention.

[0037] The desirable operating rate of the copolymerized polyester (C) used for this invention in consideration of this point is 0.04 - 40 % of the weight more preferably 0.01 to 60% of the weight to the whole drainage system poly aniline constituent of this invention. When neither reinforcement when the rate considers as a thin film at less than 0.01 % of the weight, nor flexibility is fully acquired and it exceeds 60 % of the weight, conductivity falls and it is lacking in practicality. As for the conductivity of the constituent after mixing, it is desirable that it is more than 10-12 S/cm. Furthermore, desirable conductivity is 10 to 9 or more S/cm.

[0038] The desirable operating rate of the water (D) used for this invention is 20 - 99.7 % of the weight more preferably five to 99.7% of the weight to the whole drainage system poly aniline constituent of this invention. This drainage system poly aniline constituent is applied to various base materials as it is less than 5 % of the weight, and in case the rate forms a thin film etc., it is inferior to processing **** or handling nature.

[0039] In the drainage system poly aniline constituent of this invention, since the improvement in dispersibility of this constituent and surface tension are reduced further, a water-soluble organic solvent (E) and a surfactant (F) can be added.

[0040] As an example of a water-soluble organic solvent (E), polar solvents, such as carboxylic acids, such as ketones, such as nitril, such as alcohols, such as ether, such as a tetrahydrofuran and dioxane, a methanol, ethanol, propanol, ethylene glycol, a glycerol, and 2-butoxyethanol, and an acetonitrile, and an acetone, a formic acid, an acetic acid, and a propionic acid, N-methyl pyrrolidone, dimethylformamide, and dimethyl sulfoxide, can be used, for example. In this case, a corrosive and toxic low thing is desirable.

[0041] When using a water-soluble organic solvent (E), the desirable operating rate is 0 - 65 % of the weight more preferably zero to 90% of the weight to the whole aqueous poly aniline constituent of this invention. If the rate exceeds 90 % of the weight, volatilization of an organic solvent will be remarkable at the time of paint film desiccation etc., and will pose an environmental sanitation top problem at it.

[0042] Moreover, although it will not be limited as a class of surfactant (F) especially if the dissolution and distribution of doping of the poly aniline, the poly aniline, and polyester are not blocked, but an anion system, a cation system, and the Nonion system surfactant are used, the Nonion system surfactant is used preferably.

[0043] When using a surfactant (F), the desirable operating rate is 0 - 3 % of the weight more preferably zero to 5% of the weight to the whole aqueous poly aniline constituent of this invention. If the rate exceeds 3 % of the weight, the water resisting property and reinforcement of a thin film which are obtained may fall.

[0044] The drainage system poly aniline constituent of this invention is manufactured including the process of following the (1) - (3) at least.

(1) The process which makes water and/or a water-soluble solvent dissolve or distribute the poly aniline and/or its derivative (A), and a proton acid dopant (B).

(2) The process which makes water and/or a water-soluble solvent dissolve or distribute copolymerized polyester (C).

(3) The process which mixes the solution or dispersion liquid prepared by the above (1) and (2).

In addition, water is not contained in the mixed liquor obtained at the process in the above (3), or when there is little water, water can be added suitably, and if, a solvent is also removable from mixed liquor. Furthermore, when adding a surfactant as occasion demands, it can add into mixed liquor at the time of the arbitration of the above-mentioned process.

[0045] A conductive thin film is obtained on a base material front face by making a base material apply and dry the drainage system solution or dispersion liquid containing the constituent of this invention. There is no limitation special to the base material used. As a base material, they are a resin fabrication article, plastic film, a synthetic paper, fiber, a metal, etc. Especially the material of a resin fabrication article is not limited, but polyester, polystyrene, polyethylene, a polyamide, a polyvinyl chloride, polyvinyl acetate, polypropylene, a styrene-butadiene copolymer, polybutadiene, a polysiloxane, a polycarbonate, a polyacrylonitrile, polymethylmethacrylate, ABS plastics, etc. are mentioned, and, specifically, there is no limitation also in a configuration. Polyester, polyethylene, polypropylene, a polyamide, a polycarbonate, etc. are mentioned as a material of plastic film. The thing of polyester and a polypropylene system is mentioned as a synthetic paper. As fiber, it is a natural fiber, a chemical fiber, a synthetic fiber, an inorganic fiber, etc., and, specifically, there are inorganic fibers, such as synthetic fibers, such as chemical fibers, such as natural fibers, such as cotton,

hemp, wool, and silk, and rayon, and polyester polyamide acrylic polyethylene polypropylene polyurethane, and a glass fiber, a carbon fiber, etc. As a metal, there are especially steel, stainless steel, aluminum, etc. and it is not limited.

[0046] There is especially no limitation about the approach of making a thin film forming on a base material front face. The constituent of the poly aniline and copolymerized polyester of this invention is applied by the solution or dispersion liquid, and a base material is applied by the approach of immersion, brush coating, a roller coat, a spray coat, etc., and thin film formation is easily possible by making it dry, and it can apply also to the base material of a large area and a long picture.

[0047] Especially the thickness of a thin film is not limited but is suitably chosen from the surface-electrical-resistance value demanded and the conductivity of this constituent. When covering the constituent of the same conductivity, thickness and a surface-electrical-resistance value have the relation of an inverse proportion. Generally, 10 micrometers - ten to 4 micrometer is desirable. Thus, as for the conductivity of the obtained thin film, it is desirable that it is more than 10-12 S/cm. Still more desirable conductivity is 10 to 9 or more S/cm.

[0048]

[Effect of the Invention] The description of the drainage system poly aniline constituent of this invention is in the point of using a copolymerized polyester (C) component, it is that the 2 - 35-mol % is sulfonic-acid metal salt content aromatic series dicarboxylic acid as a component with the especially desirable polycarboxylic acid component in this copolymerized polyester, and this copolymerized polyester is closed if it is water solubility or water-dispersion. A drainage system can be made to dissolve or distribute the poly aniline by mixing the poly aniline to such copolymerized polyester now. Thus, from the solution or dispersion liquid of the obtained constituent, a thin film can be easily formed by spreading and desiccation.

[0049] This conductive thin film has the following descriptions, and is very useful as antistatic film, such as a resin fabrication article, plastic film, a synthetic paper, and fiber, and a metaled corrosion prevention coat. i) -- ii transparency with few humidity dependencies of conductivity is excellent -- v with iv water resisting property and weatherability high since it is a thin film on an iii front face which do not spoil the dynamic physical properties of base material original -- conductivity is comparatively high and the possibility of surface electrical resistance (103-1010ohms / **), vi solution, or dispersion liquid of arbitration is a drainage system.

[0050]

[Example] Although an example is given to below and this invention is explained to it, this invention is not limited at all by these examples. The appraisal method used for this invention is shown below. [0051]

Conductivity: It measured by the one terminal pair network method under applied-voltage 500V and a 25-degree C condition with the specific resistance measuring instrument by Takeda Riken.

[0052] adhesion: -- after mincing the squares with the cutter knife on the surface of the thin film and sticking a cellophane tape, it exfoliated and the number which remained among 100 measure eyes was counted.

[0053] Pencil degree of hardness: It examined by the existence of a 200g [of loads] blemish by JIS-K-5401 law using the pencil length **** test coupon.

[0054] Synthetic example 1 aniline 15g, 270g of distilled water, and 36g of concentrated hydrochloric acid were added, and after the zero temperature solution which dissolved 24.5g of ammonium persulfates in 70g of distilled water while keeping at degree C was dropped in 1 hour, it agitated for further 4 hours. After carrying out the ** exception and performing rinsing, a methanol, and ether washing, the vacuum drying was carried out and poly aniline 12.4g was obtained. After adding 10g of the obtained poly aniline to 1000g of aqueous ammonia 3% and agitating at a room temperature for 2 hours, it carried out the ** exception and rinsing, methanol swabbing, and ether washing were performed. The vacuum drying was carried out and the 6.5g dedope poly aniline (EMERARU gin base) was obtained. When it was made to dissolve in N-methyl pyrrolidone and GPC was measured, they were number average molecular weight 27000 and weight average molecular weight 99000 in polystyrene conversion.

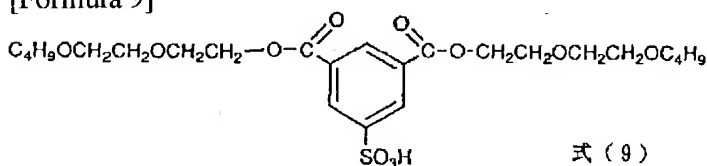
[0055] 0.067g of zinc acetate was added to 300ml 3 opening flask equipped with a synthetic example 2 churning machine, distilling-off object draw tubing, and a thermometer as 5-sulfo sodium isophthalic acid dimethyl 27.8g, diethylene-glycol-Monod n-butyl ether 207.8, and an esterification catalyst, and it reacted at 210 degrees C for 8 hours. Along with reaction advance, it became a transparence homogeneity liquid from white suspension, and the methanol of computational complexity distilled. Unreacted diethylene-glycol-Monod n-butyl ether was distilled by 220 more degrees C and 70mmHg in 2 hours.

[0056] 20g (the ORGANO CORP. make, Amberlyst 15) of ion-exchange resin was added to 30ml of THF solutions of 2g of diester compounds obtained in the example 2 of synthetic example 3 composition, and it

agitated at the room temperature for 15 minutes. After filtering with a glass filter, ion exchange resin was again washed by THF 30ml, and was set by the filtrate. It titrated in the sodium-hydroxide water solution of 0.02 conventions, and confirmed that the sulfo sodium group was quantitatively changed into sulfonic-acid residue. THF is distilled off and a residue is dried – the structure of a formula (9) was checked by ¹H-NMR and IR.

[0057]

[Formula 9]



[0058] When ultrasonic irradiation of dedope poly aniline 0.10g and the 0.30g (formula (9)) of the above-mentioned sulfonic acid type diester compounds obtained in the synthetic example 1 was added and carried out to THF 8ml, the solution of uniform dark green was obtained in 3 hours. When this solution was filtered with the glass filter, the insoluble matter which remained on the filter was very little. Applied this dope condition poly aniline THF solution on the polyethylene terephthalate film, it was made to dry at 120 degrees C for 1 hour, and the thin film of 1 micrometer of thickness was obtained. It was $\sigma=13$ (S/cm) when conductivity was measured about the obtained thin film. The dope condition poly aniline was dissolved in 2-n-butoxy-ethanol by the same approach, and the thin film was made to form. It was conductivity $\sigma=9$ (S/cm).

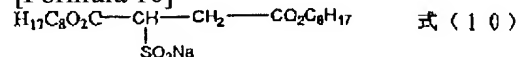
[0059] The synthetic example 42, 2'-dinaphthyl methane -6, and 1g of 6'-disulfon acid sodium salt were melted to 30ml of distilled water, 30g (Amberlite IR-120B) of ion-exchange resin was added, and it agitated for 15 minutes at the room temperature. The glass filter washed ion exchange resin twice by 30ml of distilled water the back according to **, and it united with the filtrate. It titrated in the sodium-hydroxide water solution of 0.02 conventions, and confirmed that the sulfo sodium group was quantitatively changed into the sulfonic group. 2, 2'-dinaphthyl methane -6, and 3g of 6'-disulfon acid sodium salt were added and melted in the water solution, and it agitated at the room temperature for 30 minutes, and considered as the dopant solution.

[0060] 70ml of dopant solutions of the synthetic example 4 and aniline 0.3g were put into 3 opening flask 300ml equipped with the synthetic example 5 churning machine and the thermometer, and it cooled at 0 degree C. It cools at 0 degree C beforehand, and 10ml of water solutions of 0.6g of ammonium peroxydisulfates which are a polyacid-ized agent was dropped in 10 minutes. The reaction mixture was kept at 0 degree C, and was agitated for 20 hours. Although the generated dope poly aniline was dissolved, it dialyzed for two days as it is (the product made from Spectrum Medical Industries, the spectra/pore 7, FE-0521-05). Some solutions were dried and solid content concentration was determined. Applied this dope condition poly aniline water solution on the polyethylene terephthalate film, it was made to dry at 120 degrees C for 1 hour, and the thin film of 1 micrometer of thickness was obtained. When conductivity was measured about the obtained thin film, it was $\sigma=2.2 \times 10^{-3}$ (S/cm). When this poly aniline 0.1g was processed at the room temperature by 10ml of aqueous ammonia 3% for 2 hours, it rinsed and dried the ** exception, the dedope poly aniline was dissolved in NMP and GPC was performed, in polystyrene conversion, number average molecular weight was 12000 and weight average molecular weight was 23000.

[0061] 3g [of sulfonic-acid sodium salt compounds of synthetic example 6 formula (10)], 0.4ml [of concentrated hydrochloric acid], and aniline 0.47g and 15ml of distilled water were mixed in 100ml 3 opening flask, and it cooled at 0 degree C. It cools at 0 degree C beforehand, and 5ml of water solutions of 1.15g of ammonium peroxydisulfates which are a polyacid-ized agent was dropped at the above-mentioned mixture in 10 minutes. The reaction mixture was kept at 0 degree C, and was agitated for 20 hours. It was distributing and the generated dope poly aniline was not made a ** exception. It dialyzed for two days then (the product made from Spectrum Medical Industries, the spectra/pore 7, FE-0521-05).

[0062]

[Formula 10]



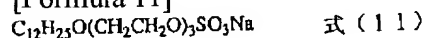
[0063] Some solutions were dried and solid content concentration was determined. Applied this dope condition poly aniline water solution on the polyethylene terephthalate film, it was made to dry at 120 degrees C for 1 hour, and the thin film of 1 micrometer of thickness was obtained. When conductivity was measured about the

obtained thin film, it was $\sigma = 1.2 \times 10^{-2}$ (S/cm). When this poly aniline 0.1g was processed at the room temperature by 10ml of aqueous ammonia 3% for 2 hours, it rinsed and dried the ** exception, the dedope poly aniline was dissolved in NMP and GPC was performed, in polystyrene conversion, number average molecular weight was 13000 and weight average molecular weight was 28000.

[0064] The compound of (14) was used instead of the compound of a formula (10) from the formula (11) like the synthetic example 7, and the poly aniline was compounded. The conductivity of the generated poly aniline and average molecular weight are shown in Table 1.

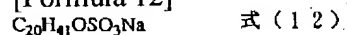
[0065]

[Formula 11]



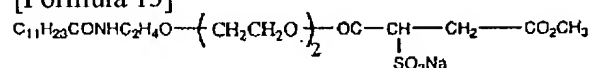
[0066]

[Formula 12]



[0067]

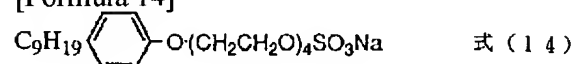
[Formula 13]



式 (13)

[0068]

[Formula 14]



[0069]

[Table 1]

化合物番号	導電率 (S/cm)	Mn	Mw
式 (11)	2.9×10^{-2}	12000	28000
式 (12)	1.7×10^{-2}	13000	26000
式 (13)	6.7×10^{-2}	11000	27000
式 (14)	1.4×10^{-2}	12000	25000

[0070] To the glass reactor to which a synthetic example 8 churning machine, nitrogen installation reduced pressure tubing, and a thermometer were attached, 5-sulfo sodium isophthalic acid G beta-hydroxyethyl 10.3g (29mmol), Isophthalic acid G beta-hydroxyethyl 20.8g (82mmol), Terephthalic-acid G beta-hydroxyethyl 20.8g (82mmol), polyethylene-glycol (mainly tetramer) 11.6g (60mmol) and 14mg of antimony oxide were added, and nitrogen gas permuted the inside of a reactor enough -- afterbaking was carried out, reduced pressure was started from 260 degrees C, and it decompressed to 0.3mmHg(s) over 30 minutes. Terminal temperature is 275 degrees C, continued heating and reduced pressure as it was for 3 hours, and made it react. When it took out after cooling and GPC was performed by using N-methyl pyrrolidone as a solvent, number average molecular weight was 11000 in polystyrene conversion. When the presentation was analyzed by ¹H-NMR, for 42.5-mol % and a terephthalic acid, ethylene glycol was [5-sulfo sodium isophthalic acid / 15.0 mol % and isophthalic acid / 70.0 mol % and a polyethylene glycol (mainly tetramer)] 30.0-mol % among [42.5 mol % and all] the polyol component among [all] the polycarboxylic acid component.

[0071] 2.13g of sodium acetate was added to 500ml 3 opening flask equipped with a synthetic example 9 churning machine, a condensator, distilling-off object draw opening, and a thermometer as 48.5g [of dimethyl terephthalates] (0.250 mols), and isophthalic acid dimethyl 46.0g (0.237 mols), 5-sulfo sodium isophthalic acid dimethyl 3.7g (0.013 mols), ethylene glycol 23.4g (0.375 mols), neopentyl glycol 39.0g (0.375 mols), and a reaction catalyst, and it be made to react to it at 200 degrees C for 4 hours Along with reaction advance, it became transparence homogeneity liquid from white suspension, and the methanol of computational complexity distilled. the glass reactor to which a churning machine, nitrogen installation reduced pressure tubing, and a

thermometer were attached after cooling the above-mentioned mixture -- moving -- as a polycondensation catalyst -- 11.6g of antimony oxide -- in addition, nitrogen gas permuted the inside of a reactor enough -- afterbaking was carried out, reduced pressure was started from 260 degrees C, and it decompressed to 0.3mmHg(s) over 30 minutes. Terminal temperature was 275 degrees C. It was made to react then for 3 hours. [0072] When it took out after cooling and GPC was performed by using N-methyl pyrrolidone as a solvent, number average molecular weight was 12000 in polystyrene conversion. When the presentation was analyzed by ¹H-NMR, for 47.5-mol % and a terephthalic acid, ethylene glycol was [5-sulfo sodium isophthalic acid / 2.5 mol % and isophthalic acid / 50.0 mol % and neopentyl glycol] 50.0-mol % among [50.0 mol % and all] the polyol component among [all] the polycarboxylic acid component. 34.0g of copolymerized polyester and 2-n-butoxy ethanol 10.8g obtained by the glass reactor to which the churning machine and the thermometer were attached were added, and it heated at 120 degrees C, and was made to dissolve in homogeneity. After cooling mixed liquor at 100 degrees C, agitating violently, when 55g of water was dropped little by little, it became dispersion liquid.

[0073] The THF solution of the dope poly aniline of the example 3 of example 1 composition and the THF solution of the copolymerized polyester of the synthetic example 8 were mixed at a various rate, and when distilled water was added little by little, carrying out ultrasonic irradiation to mixed liquor further, a dope poly aniline and copolymerized polyester were distributed. Ultrasonic irradiation was then continued for 2 hours, and THF was distilled off. A dope poly aniline and copolymerized polyester were distributing after THF distilling off, and sedimentation was not seen. In this way, the obtained dispersion liquid were made to apply, dry and thin-film-ize on a polyethylene terephthalate film (1 micrometer of thickness), and conductivity was measured. The conductivity change to the weight ratio of the poly aniline is shown in drawing 1. When the thin film was observed with the optical microscope (400 times), phase separation was not seen in which rate. When the percentages of a dope poly aniline were 10, 20, 30, and 50wt%, the adhesion of a thin film was 100% and the pencil degree of hardness was 2H.

[0074] The water solution of the dope poly aniline of the example 5 of example 2 composition and the dispersion liquid of the copolymerized polyester of the synthetic example 9 were mixed at a various rate. A dope poly aniline and copolymerized polyester resin were distributed, and sedimentation was not seen. In this way, the obtained dispersion liquid were made to apply, dry and thin-film-ize on a polyethylene terephthalate film (1 micrometer of thickness), and conductivity was measured. The conductivity change to the weight ratio of the poly aniline is shown in drawing 1. When the thin film was observed with the optical microscope (400 times), phase separation was not seen in which rate. When the percentages of a dope poly aniline were 20, 30, and 50wt%, the adhesion of a thin film was 100% and the pencil degree of hardness was 2H.

[0075] The water dispersion of the dope poly aniline of the example 6 of example 3 composition and the dispersion liquid of the copolymerized polyester of the synthetic example 9 were mixed so that the weight ratio to the total solids of a dope poly aniline might become 30%. A dope poly aniline and copolymerized polyester resin were distributed, and sedimentation was not seen. In this way, the obtained dispersion liquid were made to apply, dry and thin-film-ize on a polyethylene terephthalate film (1 micrometer of thickness), and conductivity was measured. It was conductivity $\sigma=3.6 \times 10^{-3}$ (S/cm). Phase separation was not seen when the thin film was observed with the optical microscope (400 times). The adhesion of a thin film was 100% and the pencil degree of hardness was 2H.

[0076] The water dispersion of a dope poly aniline (synthetic example 7 reference) and the copolymerized polyester dispersion liquid of the synthetic example 9 which were compounded using the compound of (14) from example 4 formula (11) were mixed so that the weight ratio to the total solids of a dope poly aniline might become 30%. It was made to thin-film-ize like an example 3, and conductivity was measured.

[0077]

[Table 2]

化合物番号	導電率 (S/cm)
式 (11)	4.1×10^{-3}
式 (12)	3.2×10^{-3}
式 (13)	6.7×10^{-3}
式 (14)	2.9×10^{-3}